

## X-Ray Diffraction Studies of Leather

By S. D. BAILEY AND V. F. ALBERT

In the course of an investigation of methods suitable for the determination of the extent and causes of the deterioration of leather, the x-ray diffraction patterns of a number of new and deteriorated samples of leather were made. In the comparison of these diffraction patterns to those reported in the literature (1), we were impressed by the fact that none of the literature diffraction patterns show the reflections due to the additives. A probable explanation of this is that x-ray studies in the past have been made with the primary purpose of determining the effect of tanning agents on the reflection spacings of the collagen fibers.

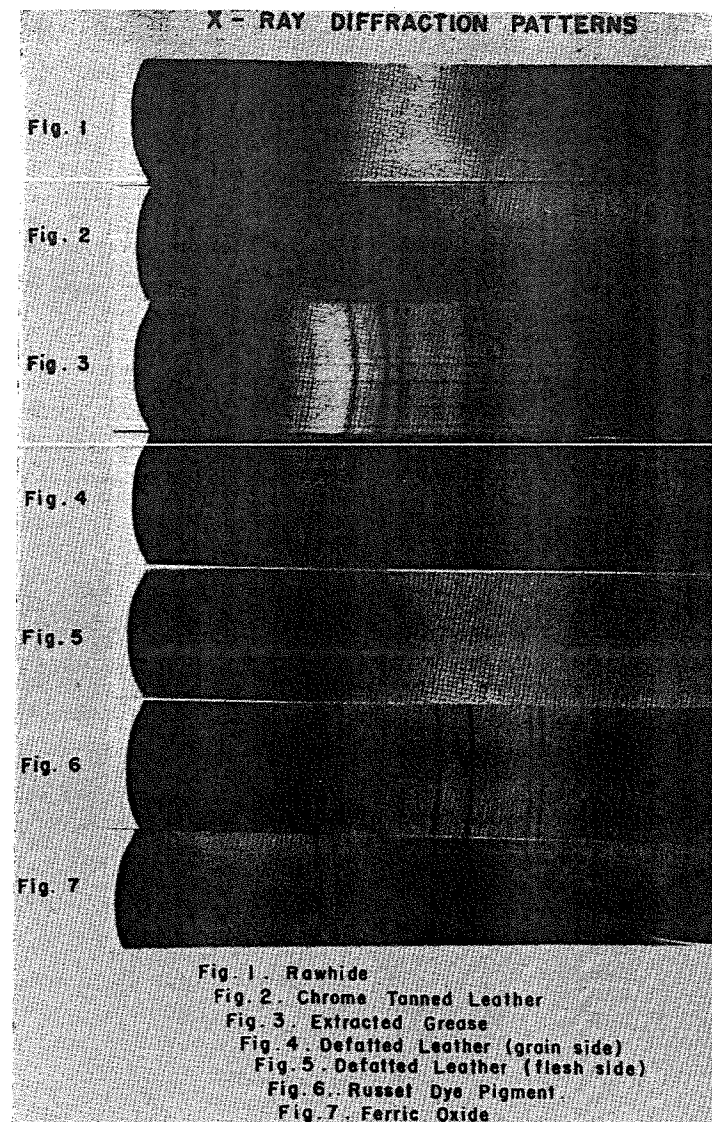
Collagen is characterized by three principle reflections—the equatorial reflection of 11.5 Å, a diffuse equatorial reflection the center of which is at 4.4 Å, and the strong meridional arc of 2.86 Å. These spacings are shown in the x-ray photograph of a sample of rawhide, Figure 1 from the present study. The very faint reflection of 6.9 Å and of 2.06 Å (not perceptible in the reproduced patterns) conform with predicted spacings of the three-chain helix structure proposed by Pauling and Corey (2) for the collagen protein. While the collagen polypeptide chain serves as the basic network of leather fiber bundles, collagen alone has little resemblance to the completed leather product. This conversion, mostly physical in nature, is brought about in the various steps of leather manufacturing by the addition of tanning agents, stuffing greases and finishing dyes. Such additives may constitute as much as 30-40 percent of the dry weight of the finished product and, therefore, contribute to those properties of leather which may be expected to undergo change upon deterioration. Methods capable of studying the components of leather without resorting to their extraction would be most valuable in the attempts to explain the chemical and physical changes taking place in the manufacture of leather and as leather deteriorates during unfavorable storage conditions.

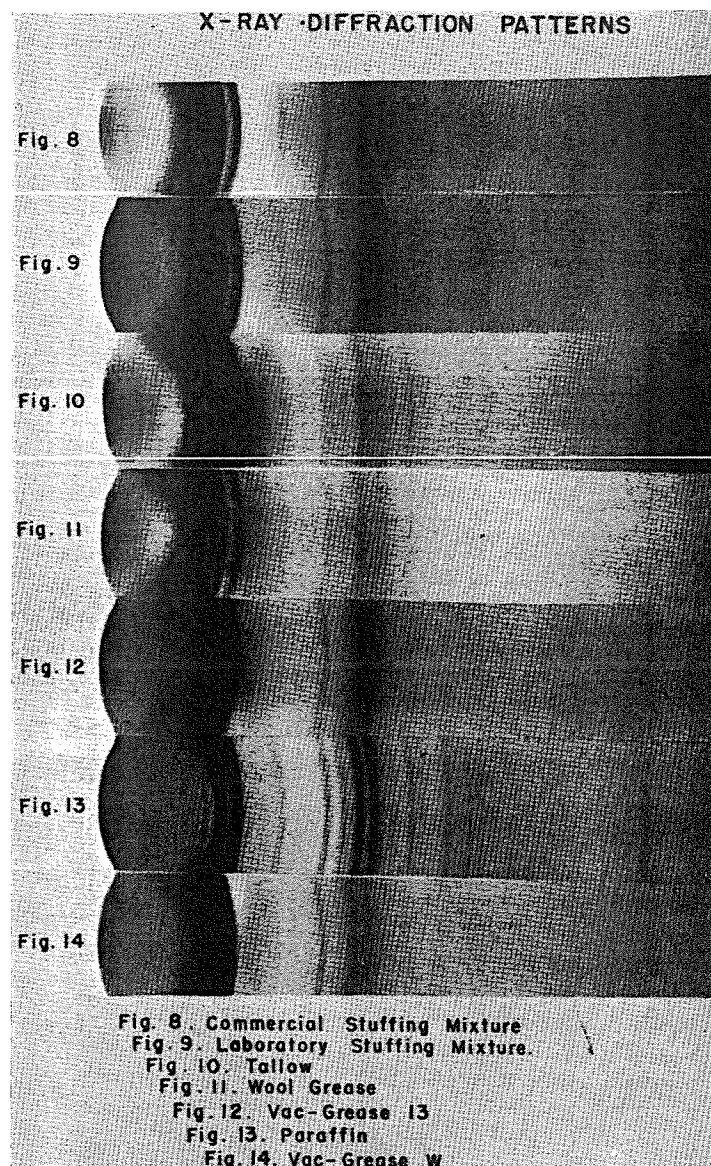
Samples of chrome retan upper leather prepared according to Military Specification MIL-L-3122 have been used in this study. The desired level of chemical composition as given by this specification is 22 to 25 percent grease, 4.5 to 5.5 percent chromium (reported as chromic oxide) and 40 to 50 percent vegetable tannins, computed on a hide substance basis. In addition, it is required that the leather shall be dyed and finished on the grain side to a russet color.

A General-Electric XRD-I instrument producing nickel filtered copper  $K\alpha$  radiation and equipped with a 14.32 cm powder camera, was used in obtaining the diffraction patterns of the figures. Samples of the leather were cut into slivers measuring approximately 2 mm by 10 mm. These were supported in the oscillating mount of the powder camera. Grease samples were similarly supported in a wedge shaped holder. The diffraction pattern of a sliver of this chrome retan leather mounted so that the upper surface (grain side) intercepted the beam is shown in Figure 2. A comparison of this pattern to that of the rawhide (Figure 1) clearly indicates the presence of crystalline material capable of producing reflections to a much greater extent than collagen. To explain these additional reflections of a non-collagenous origin, a sample of the same leather was exhaustively extracted with chloroform using the method of Zimmerman and Pangborn (3). The extracted, solvent free grease, constituting 20.4 percent of the dry weight of the leather, gave the diffraction pattern of Figure 3. Several of the arcs of the intact leather pattern, Figure 2, may be shown to be due to these grease reflections. The defatted leather remaining from the grease extraction gives all of the reflections (Figure 4) of the intact leather with the exception of those attributable to the grease. Since this leather sample was taken from the grain side, an examination of the diffraction patterns on the flesh side and inner portions of the leather were made. Figure 5 shows the pattern obtained on the same defatted sample of Figure 4, with the exception that the flesh side surface was exposed to the x-ray beam. The absence of these arcs in the flesh surface clearly points to a crystalline material in the grain side. Since the leather sample was made according to specifications requiring a russet finish, it was readily shown that the pigments of the surface finishing material used in producing the russet color, gave a diffraction pattern (Figure 6) the reflections of which coincide with this grain side pattern. In turn, these were shown to be primarily due to the presence of ferric oxide ( $Fe_2O_3$ ), identified through the use of the ASTM x-ray card file, as shown by Figure 7.

Thus, most of the diffraction spacings of the chrome retanned leather have been assigned either to the stuffing grease or the finishing surface material. Three arcs, however, of moderate intensity at spacings of 3.38, 3.26 and 2.98 Å, are yet to be explained. It may be possible to assign these to the tanning compounds, particularly, chromium compounds which would be expected to have well defined diffraction patterns.

The extracted grease appears identical as far as x-ray diffraction





is concerned, to commercial stuffing mixture (Figure 8) and to a laboratory stuffing mixture (Figure 9), consisting of 30 percent Vac-Grease W, 30 percent Vac-Grease 13 (hard), 20 percent wool grease, 11 percent tallow, 5 percent moellen-waterless and 4 percent paraffin. The diffraction pattern of these components are shown separately in Figure 10 to Figure 14. Similarities in these diffraction patterns, particularly the short spacings in the region from 3.7-4.2A, have been noted previously (4) as typical of a large number of fats, oils and waxes.

#### CONCLUSIONS

The x-ray diffraction pattern of russet dyed leather consists of reflection arcs due to pigments of the surface dye, stuffing greases, and the spacings of the collagen polypeptide chain. Where changes resulting from the deterioration of leather involve these substances, x-ray diffraction will provide a qualitative method for its evaluation. No reflection arcs have been observed for the tanning agents, though three arcs have yet to be accounted for.

A comparison of new and deteriorated leathers by x-ray diffraction is being presently investigated.

#### References

1. Lloyd, D. J., J. Int. Soc. Leather Trade Chem 19, 336, 345 (1935).  
Highberger, J. H. and H. J. Kirsten, J. Am. Leather Chem. Assoc., 33, 16 (1938).  
Bear, Richard S., J. Am. Leather Chem. Assoc. 46, 438 (1951).  
Chesley, K. G., H. V. Anderson, E. R. Theis, J. Am. Leather Chem. Assoc. 27, 12 (1932).  
Bear, R. S., O. E. Bolduan, T. T. Solo, J. Am. Leather Chem Assoc. 46, 107 (1951).
2. Pauling, L., and R. B. Corey, Proc. Natl. Acad. Sci., 37, 272 (1951).
3. Zimmerman, E. W. and E. F. Pangborn, J. Am. Leather Chem. Assoc. 46, 342 (1951).
4. Bailey, A. E., Chap. III, Melting and Solidification of Fats, Inter-science Publishers, Inc., N. Y. (1950).

#### ACKNOWLEDGMENT

The authors acknowledge the assistance of Mr. E. T. Steiner and Mr. E. C. Dogliotti in supplying leather samples used in this study and for making the grease extraction.

#### PIONEERING RESEARCH LABORATORIES

PHILADELPHIA QUARTERMASTER RESEARCH AND  
DEVELOPMENT LABORATORIES  
PHILADELPHIA, PA.